X-RAY SNAPSHOTS OF POLYMERS

Revealing Structure on a Microscopic Scale

While they may look uniform to the eye, most of the materials that find their way into our high-tech world are actually complicated mixtures when viewed under the right kind of microscope. Polymer materials, such as plastics, are no exception. Moreover, the physical and chemical properties, such as the combination of strength with light weight and the resistance to corrosive substances, that make polymers attractive depend critically on the multiple components making up the mixtures. So does the all-important manufacturing cost.

Polyurethane Foams

Among polymers, polyurethanes are particularly versatile because chemical manufacturers can tailor them in several distinct forms with different physical and chemical properties. Among these are both flexible and rigid foams used to make products as diverse as seat cushions, bedding, building insulation, and lightweight structural parts. Polyurethane foams are chemically complex materials formed by the reactions of liquid starting ingredients (isocyanates and polyethers). The foamy structure results from the release of carbon dioxide bubbles generated by a reaction of water with the isocyanate. Other chemical reactions that convert the soup of initial ingredients into a polymer also influence the final structure and physical properties.

On a microscopic scale, polyurethane foam comprises a matrix laced with small particles that either form naturally during the fabrication process or are added deliberately. Since the microstructure (concentration, size distribution, and chemical composition) of the particles can influence the foam's properties, chemical producers often add inexpensive filler materials to yield a material with improved hardness, strength, and "foaminess." Common fillers include styrene acrylonitrile (SAN) and urethane-based polyisocyanate polyaddition (PIPA) particles. Determining the chemical composition of individual filler particles is difficult, owing to their minute size and their sensitivity to radiation damage by x-ray or electron beams, as well as the chemical complexity of the polyurethanes. To address these issues, a team of researchers working at the ALS turned to the x-ray microscope.

Spectroscopic Imaging

X-ray microscopes at the ALS offer several advantages over conventional instruments. The higher resolution due to the short x-ray wavelength allows smaller structures to be imaged. But more important for dissecting polymers is that x rays are absorbed most strongly at wavelengths (absorption edges) characteristic of the elements present. Subtle differences in the positions of the absorption peaks, called chemical shifts, also indicate the chemical bonding with neighboring atoms, thereby providing a means of distinguishing closely related species in the complex polyurethanes. Moreover, researchers have found that the radiation damage with an x-ray microscope can be about 500 times less than with an electron microscope, giving more flexibility in studying the chemistry of these materials.

Owing to the high brightness of the ALS, researchers can focus an intense x-ray beam to a spot smaller than the filler particles, which can range from 0.3 μm to several microns in diameter, allowing full analysis of each particle separately. Conversely, selecting a wavelength matching an absorption peak and scanning the sample through the focused x-ray beam generates an image mapping the distribution of one chemical compound. This combination of capabilities is called spectroscopic imaging or spectromicroscopy.

A polyurethane foam with SAN and PIPA filler particles provides a case in point. The absorption spectra of these two materials, whose carbon atoms experience distinct chemical surroundings, differ only slightly. The difference is the key to using x-ray microscopy, allowing the researchers to make separate images of SAN and PIPA particles by measuring the transmitted light at wavelengths where the light is selectively absorbed by the components of interest.

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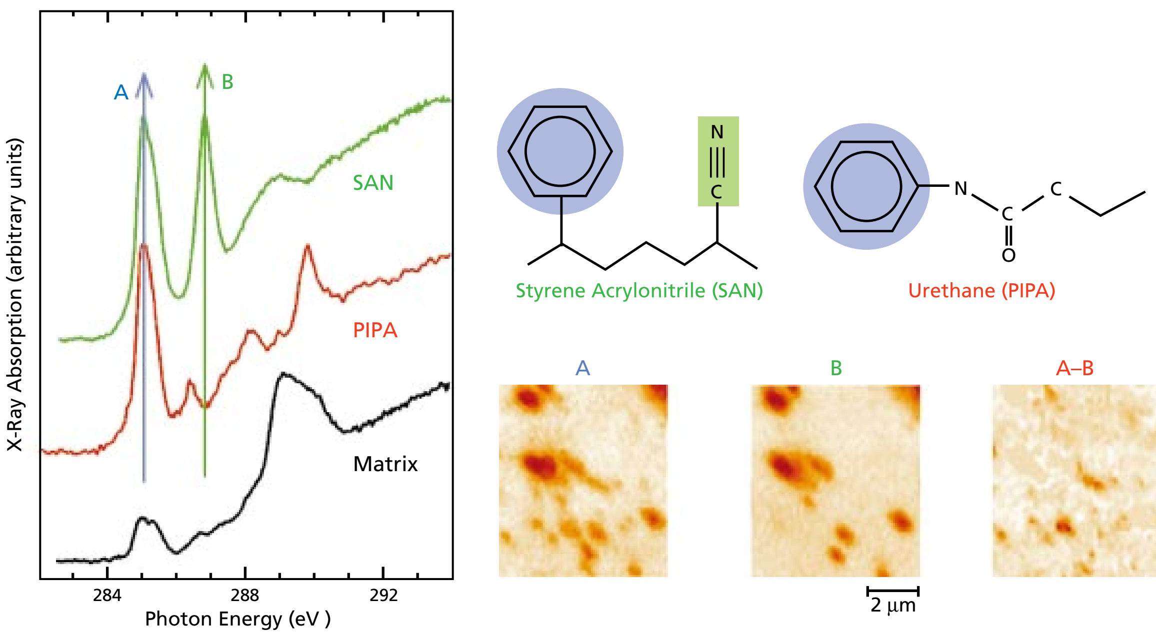

Styrene acrylonitrile (SAN) and urethane-based polyisocyanate polyaddition (PIPA) filler materials are added to customize the physical properties of polyurethane foams. The scanning transmission x-ray microscope at the ALS identifies and maps these components by illuminating the sample with x rays at wavelengths (photon energies) where the light is selectively absorbed by the components of interest. In this example, image A, recorded at a photon energy absorbed by carbon in the phenyl ring (blue), maps both SAN and PIPA. Image B, recorded at a photon energy absorbed by the carbon-nitrogen triple bond (green), shows only the SAN. Image A–B, which is the difference between the two, maps the PIPA component. The spatial resolution in these images is about 150 nm (improved to 80 nm in later experiments).